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厦门大学

MASTER DEGREE THESIS

Study on novel approaches to the synthesis of Au/TS-1 catalysts for gas-phase propylene epoxidation in the presence of O_2 and H_2

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DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
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CERTIFICATION

I, Professor_____, hereby certify that I have read this manuscript and recommend for acceptance by Xiamen University a dissertation entitled "**Study on novel approaches to the synthesis of Au/TS-1 catalysts for gas-phase propylene epoxidation in the presence of O_2 and H_2"** in fulfillment of the requirements for the award of the degree of Master of Engineering at Xiamen University, People's Republic of China.

Signed……

Supervisor

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ORIGINALITY STATEMENT

The research described in this Master of Engineering thesis was conducted under the supervision of _____ at the Department of Chemical and Biochemical Engineering, Xiamen University. I hereby declare that the work submitted is my own and that appropriate credit has been given where reference has been made to the work of others. I also confirm that it has not been previously or concurrently submitted for any other degree, diploma or any other qualifications at Xiamen University, P.R China or other institutions.

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Date:_____

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ABSTRACT

Catalysis is one front on which scientists and engineers are making a great contribution in making the production and manufacture of consumer goods both more cost effective and environmentally friendly. By developing highly specific and active catalysts, fewer undesirable byproducts will be produced thereby saving energy that would be expended in costly separation processes. In line with these efforts, high performance gold on titanium silicalite-1 (Au/TS-1) catalysts for direct gas-phase propylene epoxidation using O_2 as the oxidant in the presence of H_2 were synthesized using a novel approach that uses gold (I) thiosulfate complex as a precursor. Both bioreduction-assisted synthesis and chemical synthesis approaches were explored in this research. One-factor-at-a-time experimental design was implemented to investigate variables that influence the performance of the synthesized catalysts, namely: gold loading, $Na_2S_2O_3$:Au mole ratio, pH, kind of acid for pH adjustment, and post-calcination temperature.

Characterization techniques such us X-ray diffraction measurements, transmission electron microscopy, UV-Visible diffuse reflectance spectroscopy and scanning electron microscopy were used to elucidate the structure and properties of the catalysts produced and confirmed the deposition of gold nanoparticles on TS-1 support. Gas chromatographs equipped with thermal conductivity detectors (TCD) and a flame ionization detector (FID) were used to analyze the composition of effluent gases from the glass tubular flow reactor during catalyst tests.

A catalyst prepared under the following conditions: 1.93 % nominal Au loading, $Na_2S_2O_3$:Au ratio of 4.30, pH 2 adjusted with HCl, and post-calcinated at 573 K, exhibited remarkable performance. With it, 11.2 % propylene conversion was attained and 63.3 % PO selectivity registered at a space velocity of 4000 ml g^{-1}_{cat} h^{-1} during catalyst tests in a 10 mm x 100 mm glass tubular flow reactor. This performance is equivalent to 7.1 % PO yield which is comparable to one of the best reported PO yields (8.4%) registered by Au/TS-1 catalysts tested under similar conditions.

This study provides an opening for further elucidation of a very promising Au/TS-1 catalyst preparation method which will go a long way in making production of polyether polyols, propylene glycols and propylene glycol ethers more environmentally

friendly and sustainable.

Keywords: Au/TS-1; propylene epoxidation; catalyst; gold thiosulfate; synthesis

摘要

科学家们和工程师们利用催化为更经济以及更环境友好地进行消费品的制造和生产作出了重大的贡献。通过发展高比表面的和高活性的催化剂，可以降低不需要的副产物的产量，进而在分离过程中减少能量消耗。与此一致，氢气存在下以氧气为氧化剂的高活性 Au/TS-1 催化剂采用一种以硫代硫酸金为前体的新方法来制备。论文探索了生物还原参加的合成法和化学合成法来制备金催化剂。利用单因素实验设计来考察金负载量、$Na_2S_2O_3$ 与 Au 的摩尔比、pH、调节 pH 的酸的种类以及焙烧温度等因素对催化剂性能的影响。

采用 X 射线衍射、透射电镜、紫外-可见漫反射光谱以及扫描电镜等表征方法来阐明所制备的催化剂的结构和性能，并证实金纳米颗粒在 TS-1 上的沉积。催化剂评价过程中通过玻璃管式反应器的气体组成利用装有热导检测器（TCD）和氢火焰检测器（FID）的气相色谱来分析。

当金的理论负载量为 1.93 %、$Na_2S_2O_3$ 与 Au 摩尔比为 4.30、用 HCl 调节 pH 为 2 以及焙烧温度为 573K 时，制备出来的催化剂性能最优异。在 10 mm x 100 mm 玻璃管式反应器中，空速为 4000 ml g^{-1}_{cat} h^{-1} 时，丙烯转化率为 11.2 %，环氧丙烷选择性为 63.3 %。此时，环氧丙烷的产率为 7.1%，接近于文献中报导的相似条件下 Au/TS-1 催化剂的最高环氧丙烷产率（8.4%）。

本论文开辟了一种制备 Au/TS-1 催化剂的新方法，大大有利于更环境友好地以及可持续地生产聚醚多元醇、丙二醇和丙二醇醚。

关键词：Au/TS-1; 丙烯环氧化；催化剂；硫代硫酸金；合成

LIST OF ABBREVIATIONS AND ACRONYMS

Au	Gold
CVD	Chemical Vapor Deposition
DP	Deposition-Precipitation
FID	Flame Ionization Detector
GC	Gas Chromatograph
HRTEM	High Resolution Transmission Electron Microscope
$Na_2S_2O_3$: Au	Sodium thiosulfate to gold (ratio)
PO	Propylene oxide
rpm	revolutions per minute
SEM	Scanning Electron Microscope
TCD	Thermal Chemical Detector
TEM	Transmission Electron Microscope
TS-1	Titanium silicalite-1
UV-Vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy
XRD	X-ray diffraction

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1.0 General Introduction

Included among some of the grand challenges for chemists and chemical engineers in the 21st century is that of understanding fully the basic chemical and physical properties of surfaces, especially those of solid catalysts[1]. With growing consensus around the world among climatologists that human activities are responsible for most of the global warming witnessed in the past two centuries[2,3], scientists and engineers are seeking ways of limiting the adverse effects of human activity by developing greener and consequently more environmentally friendly and sustainable technologies.

At the heart of this campaign is the attempt to develop highly selective and active catalysts which are intended to direct chemical reactions in such a manner as to minimize production of side-products as well as ensure that energy expended in separating products from unconverted reactants is saved through expediting the rate of reaction of raw materials in the feed. This thesis deals specifically with the development of a catalyst that maximizes the gas-phase production of propylene oxide in the presence of oxygen and hydrogen in an economically viable and environmentally friendly manner. The catalyst under development comprises gold nanoparticles supported on titanium silicalite-1 (TS-1). The rest of the chapter introduces the target product and discusses the evolution of the commercial production of propylene oxide and the efforts made over the years to make it "greener". Chapter 2 elucidates the materials and equipment used, experimental procedures followed in preparing the catalysts, characterization techniques employed and the analytical methods used in evaluating catalyst performance. Chapter 3 presents results of experimental efforts and discusses the performance of catalysts prepared using the bioreduction-assisted approach. Chapter 4 provides results of experimental work on catalysts synthesized using the purely chemical approach.